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CITATION:

Kiyama, Masao ...[et al]. The Growth of α -FeO Particles by Transformation at 200°C of Iron(III) Hydroxide in the Alkaline Media Containing Slight Amounts of Other Metal Ions. Bulletin of the Institute for Chemical Research, Kyoto University 199 ...

ISSUE DATE:

1991-02-28

URL:

<http://hdl.handle.net/2433/77359>

RIGHT:

The Growth of α -Fe₂O₃ Particles by Transformation at 200°C of Iron(III) Hydroxide in the Alkaline Media Containing Slight Amounts of Other Metal Ions

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Received October 22, 1990

The alkaline suspensions containing iron(III) hydroxide and slight amounts of one of Al(III), Cr(III), Ti(IV), Si(IV), or Sn(IV), were subjected to autoclaving at 200°C. The resulting products were examined by X-ray analysis, electron microscope, and BET surface area measurements. The size and shape of the α -Fe₂O₃ particles in the products and their distributions depended on the kind and amount of the metal ions. In the presence of Sn(IV), a part of iron(III) hydroxide was transformed into the α -Fe₂O₃ particles in which slight amounts of Sn(IV) were introduced.

KEY WORDS: Iron(III) hydroxide/ α -Fe₂O₃/ Hexagonal platelike particle/ Particle growth/ Autoclaving/ Alkaline suspension

INTRODUCTION

When an excess of alkaline solution is added to an iron(III) salt solution, a brownish and gelatinous substance, usually called iron(III) hydroxide, is formed. It is well known that the gelatinous precipitate in an alkaline medium transforms into α -FeO(OH) or α -Fe₂O₃ depending on the reaction temperature. α -Fe₂O₃ is formed at temperatures higher than those at which α -FeO(OH) is formed. The temperature at which the formation of α -Fe₂O₃ begins is governed by the reaction conditions.¹⁻⁴⁾ The transformation into α -Fe₂O₃ had been investigated in the presence of slight amounts of other metal ions such as Al(III), Cr(III), Ti(IV), Si(IV), and Sn(IV), which hardly form spinel ferrite in the alkaline media. The shape and size of the α -Fe₂O₃ particles were found to be different with the kind and the amount of the metal ions.

This paper describes the effect of such metal ions on the growth of α -Fe₂O₃ particles.

EXPERIMENTAL

Chemicals of an analytical grade were used except sodium silicate. Water glass containing 33 wt% Na₂SiO₃ used was chemical guaranteed grade. Water was deionized and distilled. An acidic solution was prepared in the 0.3 dm³ autoclave made of stainless steel, by mixing aqueous solutions of iron(III) nitrate and a required

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slight amount of $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, or TiCl_4 . To this an excess of a NaOH solution was added in a required amount. Each resulting suspension was diluted with water to 0.25 dm^3 . The alkaline suspensions containing Fe(III) and either Si(IV) or Sn(IV) were also prepared by mixing a NaOH solution containing slight amounts of either Na_2SiO_3 or Na_2SnO_3 and an iron(III) nitrate solution. A number of alkaline suspensions, each containing 1 M ($\text{M}=\text{mol/dm}^3$) excess NaOH, $(0.2-X)\text{M}$ Fe(III) and XM metal, M , ion (the total metal ions = 0.2 M), were prepared by varying the kind and the concentration of the M ion in the range 0.01 to 0.05 M. They were heated to 200°C at a rate of 4°C/min and kept at 200°C with mechanical stirring at 100 rpm for a fixed time of 4 h and then allowed to cool to room temperature. The resulting products were separated by filtration, well washed with water, treated with acetone, and then dried at 80°C in air.

The products were examined by X-ray diffraction using $\text{CoK}\alpha$ radiation (XRD) and transmission electron microscopic observation (TEM). The samples found by XRD to consist only of $\alpha\text{-Fe}_2\text{O}_3$ were subjected to BET surface area measurements using nitrogen.

RESULTS AND DISCUSSION

In order to examine the effect of the concentration of excess NaOH on the formation of $\alpha\text{-Fe}_2\text{O}_3$ at 200°C , the starting alkaline suspensions containing 0.2 M Fe(III) and one of 0.1, 0.5, or 1 M excess NaOH were subjected to autoclaving at 200°C . TEM photographs of the resulting samples are shown in Fig. 1. The orange sample prepared at 0.1 M excess NaOH was found by XRD and TEM to consist of a slight amount of fine spherical and cubic particles of $\alpha\text{-Fe}_2\text{O}_3$, besides needlelike $\alpha\text{-FeO}(\text{OH})$ particles. The values of BET surface area, S , of the reddish samples, which had been formed in the presence of 0.5 and 1 M excess NaOH, found by XRD examination to consist only of $\alpha\text{-Fe}_2\text{O}_3$, slightly decreased from 3.9 to $3.3 \text{ m}^2\text{g}^{-1}$ with an

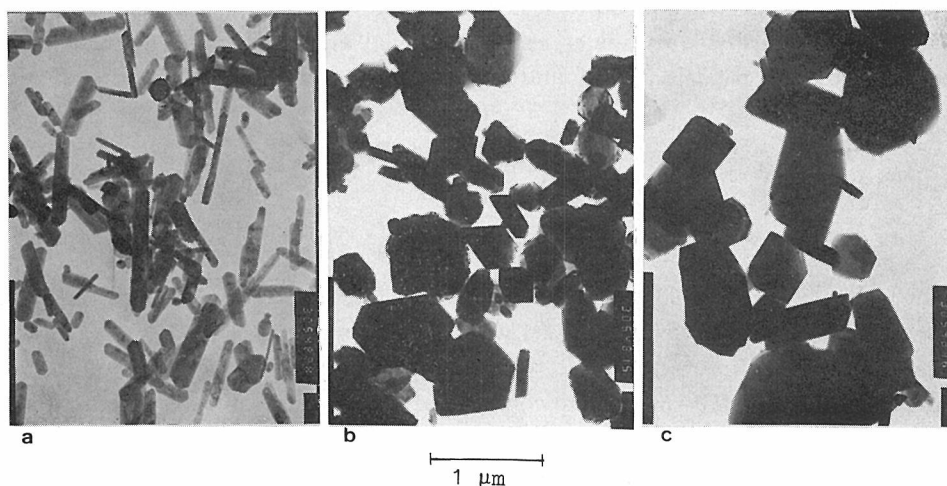


Fig. 1. TEM photographs of the samples obtained by autoclaving at 200°C alkaline suspensions containing 0.2M Fe (III) and one of 0.1 (a), 0.5(b) or 1M excess NaOH(c).

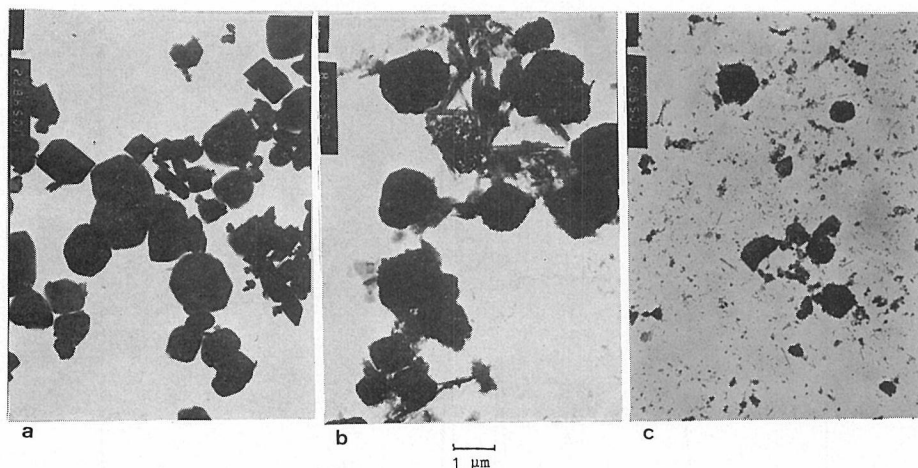


Fig. 2. TEM photographs of α -Fe₂O₃ samples obtained at 200°C in the presence of 0.18 M Fe(III), 1M excess NaOH and one of 0.02M Al (III) (a), Cr(III) (b), or Ti(IV)(c).

increase in the excess NaOH concentration.

Alkaline suspensions, each containing 1 M excess NaOH, (0.2- X)M Fe(III) and one of X M Al(III), Cr(III) or Ti(IV), were prepared, and subjected to autoclaving. TEM photographs of three typical α -Fe₂O₃ samples prepared in the presence of 0.02 M Al(III), Cr(III), or Ti(IV) are shown in Fig. 2. In the experiments in the presence of 0.01 M Cr(III), α -FeO(OH) was formed along with α -Fe₂O₃. The growth of α -Fe₂O₃ by autoclaving was locally hindered in the presence of a slight amount of Cr(III) and Ti(IV), and the S values became greater with the increase in their concentrations. The shapes of α -Fe₂O₃ particles in the reddish samples prepared in the presence of Al(III) and their S values depended slightly on the concentration of Al(III).

When similar experiments were carried out with Si(IV) and Sn(IV) in place of the above metal ions, marked differences were found in the properties of the resulting products. XRD patterns of two typical samples prepared in the presence of 0.05 M Si(IV) and Sn(IV) are shown in Fig. 3.

TEM photographs of the samples prepared in the presence of different amounts of Si(IV) are shown in Fig. 4. The S value of the samples with golden hues, in which hexagonal platelike α -Fe₂O₃ particles exist (Fig. 4(a) and (b)), increased from 9.5 to 32 m²g⁻¹ with increasing X from 0.01 to 0.02. A further increase in X from 0.02 caused a remarkable increase in S to 196 m²g⁻¹ at 0.05 M Si(IV) and a decrease in the mean diameter in the particles (Fig. 4(c)). In the XRD patterns of the samples, the diffraction peaks for the (00 l) faces in the hexagonal crystal structure of α -Fe₂O₃ became lower and wider with the increase in the X of Si(IV) as a result of the decrease in the thickness of each hexagonal particle (Fig. 3(a)).

TEM photographs of the samples prepared in the presence of different amounts of Sn(IV) are shown in Fig. 5. The S value increased from 4.1 to 80 m²g⁻¹ with increasing X from 0.02 (Fig. 5(b)) to 0.05(c). The sample, shown in Fig. 5(c),

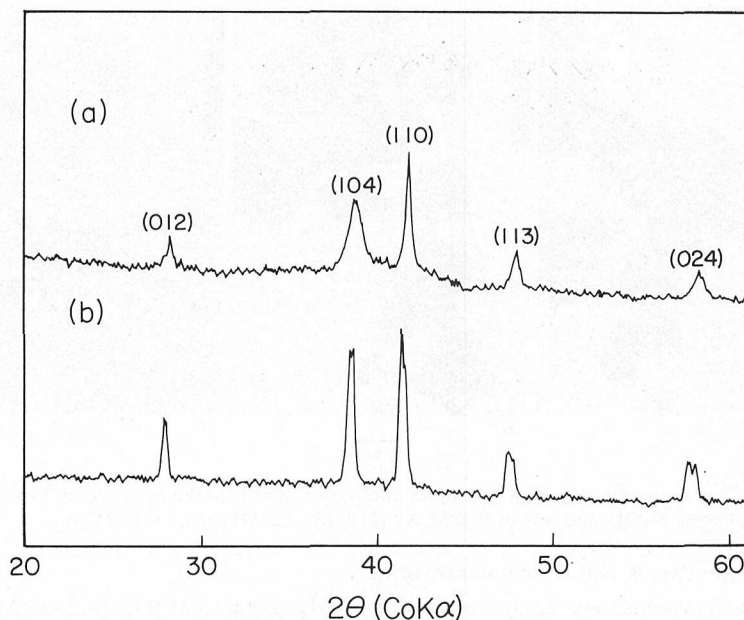


Fig. 3. XRD patterns of the samples obtained at 200°C in the presence of 0.05 M Si(IV)(a) or Sn(IV)(b).

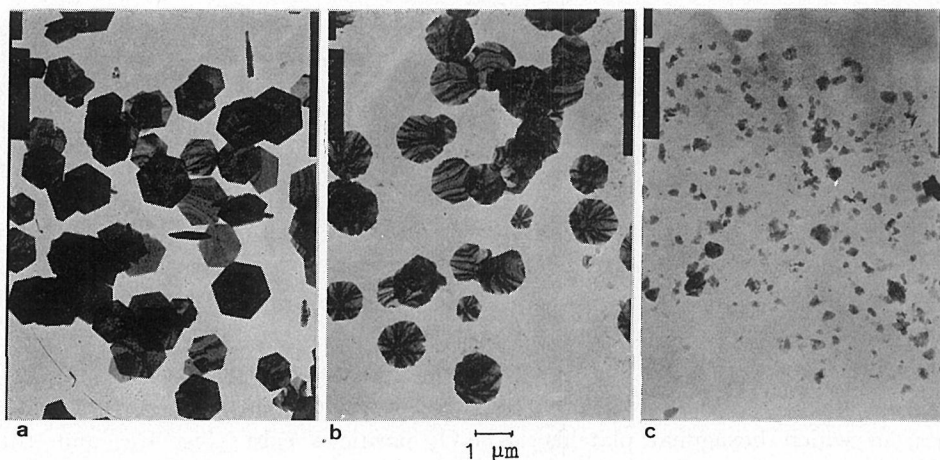


Fig. 4. TEM photographs of α -Fe₂O₃ samples obtained at 200°C in the presence of 0.01 in X(a), 0.02(b), or 0.05M Si(IV)(c).

consists of green caterpillarlike particles with extremely fine spindlelike ones besides cubic ones. Its XRD pattern (Fig. 3(b)) indicates that this sample consists of two kinds of α -Fe₂O₃ particles with slightly different lattice constants (a_0 5.04, c_0 13.78 Å and a_0 5.07, c_0 13.86 Å). When this sample was calcined in air at 800°C, the heat treated sample was found to consist of a slight amount of SnO₂ besides α -Fe₂O₃ with a_0 5.05 and c_0 13.83 Å. In order to obtain the sample consisting only of the α -Fe₂O₃ particles containing small amounts of Sn(IV) with vacancies of metal ions to

Growth of α -Fe₂O₃ Particles

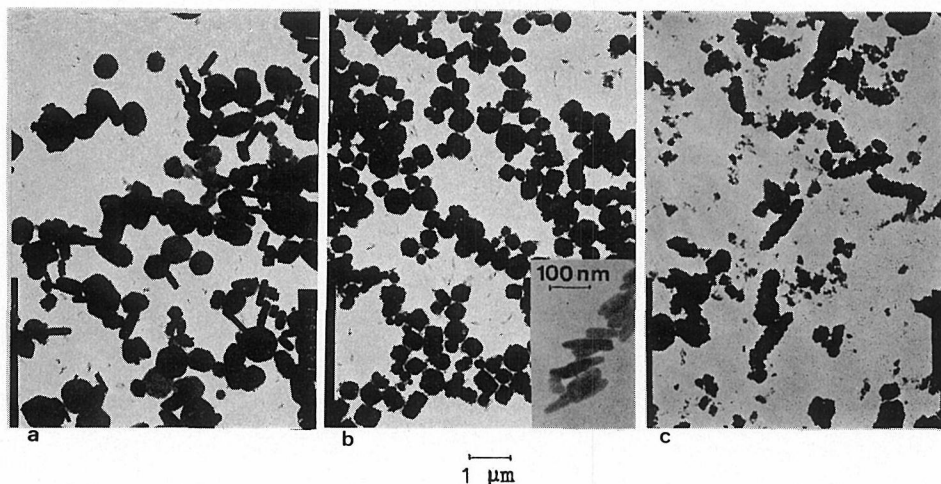


Fig. 5. TEM photographs of α -Fe₂O₃ samples obtained at 200°C in the presence of 0.01 in X(a), 0.02(b), or 0.05M Sn(IV) (c).

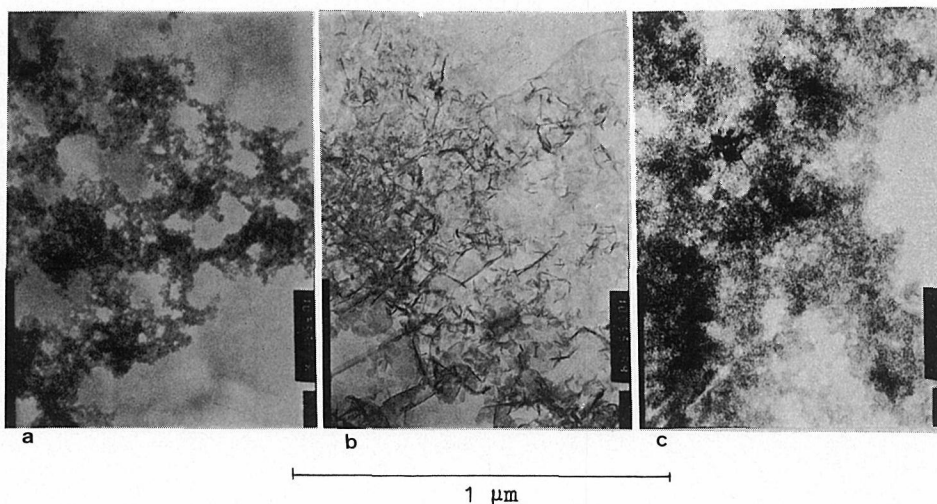


Fig. 6. TEM photographs of amorphous precipitates obtained at 200°C in the presence of 0.2M Cr(III)(a), Ti(IV)(b), or Sn(IV)(c).

keep their electronic neutrality, the alkaline suspension containing 1 M excess NaOH, 0.2 M Fe(III), and 0.2 M Sn(IV) was subjected to autoclaving at 200°C. The resulting sample with 263 m²g⁻¹ in S was shown by XRD to be amorphous.

The solubility at 200°C in 1 M excess NaOH of the metal ions used in the experiments is known to depend on their kind. When the suspensions containing 1 M excess NaOH and one of 0.2 M Al(III), Cr(III), Ti(III), Si(IV) or Sn(IV) had been subjected to autoclaving at 200°C, three kinds of amorphous precipitates containing Cr(III), Ti(IV) and Sn(IV) ions were obtained, their TEM photographs being shown in Fig. 6.

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